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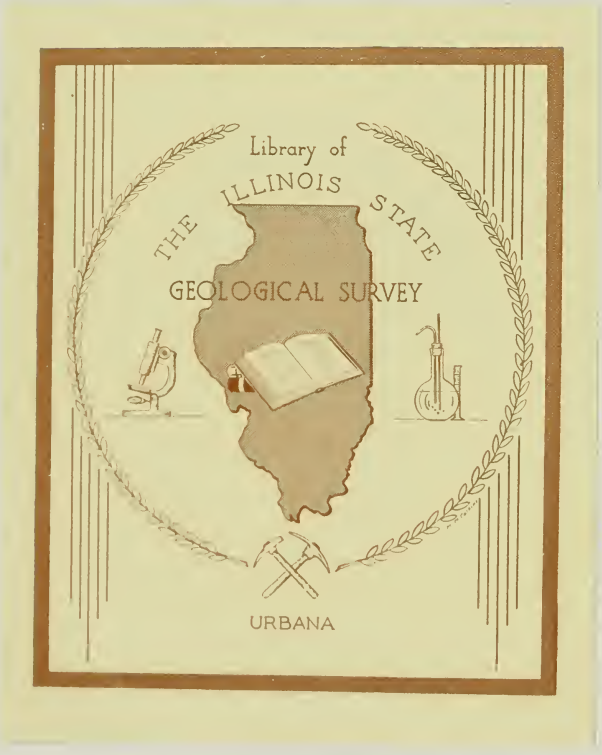
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GERMANIUM IN FLY ASH AND ITS SPECTROCHEMICAL DETERMINATION

by
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GERMANIUM IN FLY ASH AND ITS SPECTROCHEMICAL DETERMINATION

by
J. S. Machin and Juanita Witters

ABSTRACT

Thirty-four samples of fly ash from coal were collected from public utility steam power plants in Chicago and downstate Illinois to determine whether the ash were a possible source of germanium. The germanium oxide content of the ashes ranged from 0.046 to 0.004 percent. It is improbable that germanium oxide content of less than 0.1 percent would be of commercial interest. A high-voltage A.C. arc spectrochemical method used for the determination of germanium is described. A short resume of the occurrence, uses, and market for germanium is included.

PART I. INTRODUCTION

by
J. S. Machin

Historical Background

In 1871 Mendeleef, the great Russian chemist, on the basis of his periodic arrangement of the chemical elements predicted the discovery of a then unknown element. He called the element ekasilicon and predicted some of its properties. Fifteen years later Winkler found the element in the mineral argyrodite and it received the name germanium.

Germanium is estimated to be present in the earth's crust in amounts of the order of 0.1 to 0.2 ounce per ton (Goldschmidt, 1935). This is the same order of magnitude as the average concentration of arsenic, tin, and lead in the earth's crust. These metals, however, occur in relatively concentrated deposits, whereas germanium, with comparatively few exceptions, occurs thinly dispersed and associated with a variety of sulfide and silicate minerals with a preference for those types which had their origin in processes involving water at elevated temperatures and pressures (Rankama and Sahama, 1950). Carbonaceous materials, particularly coal, contain germanium in amounts of the order of a few parts per million (Goldschmidt, 1930).

The quantity of germanium in coal generally is about the same as in other sedimentary materials. Some coals, however, have a germanium content notably above average. A rather extensive survey of American coals by Stadnichenko and co-workers (1953) indicated wide distribution of germanium in our coals, but no large deposit was located in which the concentration of the metal was high enough to invite commercial exploitation under present market conditions.

Germanium has assumed increasing importance during the last 15 years owing to the development of a germanium rectifier having unusually desirable properties, and owing even more to the invention of an amplifying device which

physicists have named the transistor and which has assumed critical importance in the electronics industry. Another application of germanium that perhaps has attracted less public attention is its use in certain types of illuminating equipment to modify the character of light produced, in such a way as to make it more nearly like daylight.

Advances in the application of semiconductors (a name applied to materials having electrical characteristics similar to those of germanium) and their utilization in defense equipment during World War II and more recently in commercial and military equipment, created a growing market for germanium that has at times resulted in a market price of about $350 per pound for the refined metal. The price in July 1955 was about $250 per pound. The future outlook for the germanium market is not clear. Some competitive materials, notably silicon, have properties in some respects superior to those of germanium. It seems likely, however, that despite this competition germanium will not in the near or perhaps even the foreseeable future cease to be an important metal in the electronics industry. There have been estimates that the need for germanium in the United States in 1956 would be several times the 1953 production. It is doubtful whether the extent to which substitute materials have since entered into the picture was considered in making the estimates. In any event the shortage, if existent, was not reflected in the price as of July 1955.

The Eagle-Picher Co. has been the most important producer of germanium in the United States. This company has produced it as a by-product of their zinc operation at Henryetta, Oklahoma (Thompson and Musgrave, 1952). The production in 1953 was estimated at about three tons. There are other producers in the United States, but their production is believed to be small as yet.

In Great Britain germanium is produced almost exclusively from gas-works flue dusts (Crawley, 1955). The Japanese have produced it on a pilot-plant scale from gas-works liquor (K. Nagashima, personal communication).

The fact that germanium is widely distributed in coals and that it was successfully extracted from flue dust from gas producers in England, naturally suggested that fly ash from large coal-burning steam-generating installations might contain concentrations of germanium. This thought prompted investigation of fly ashes.

Forrest et al. (1955) examined 60 samples of dust and deposits from various types of steam power plants in England with discouraging results. They found indications of some concentration of germanium at various parts of steam-generating equipment. They found some enrichment of germanium in the fly ash from some stoker-fired equipment, but the amounts were not large enough to pay for recovery in general.

Germanium in Illinois Power Plants

Samples of fly ash were collected for our study from a number of the large steam-powered electric-generating plants located in Chicago and in several widely separated places in downstate Illinois. The samples were analyzed for germanium by a spectrochemical method developed by Witters and described in part II of this report. The results are set forth in tables 3 and 6.

One-tenth percent germanium, corresponding to about 14 hundredths percent GeO_2, tentatively may be assumed to be about the minimum amount that

might conceivably be considered of commercial interest in a fly ash. It will be seen on examination of the data that none of the fly ashes sampled contain even this minimum amount.

We found no published report of any research on the mechanism by which germanium is transported in combustion dusts or gases. The fact that it is concentrated in gas liquors and in the flue dusts in closed systems such as gas producers suggests that it may be transported as a vapor that, when it arrives at some point where the temperature conditions are favorable, condenses on any dust particles or cool surface with which it comes in contact. It is not even known in what form germanium occurs in coal. There is some evidence that it is associated with the carbonaceous part of the coal rather than with the associated minerals such as pyrite, clay, or calcite.

When more is known of the fundamentals of the mechanism of transport, it may be possible to modify the design of steam-generating equipment to favor collection of the germanium present in the fuel.

The present powdered-coal installations, which are most commonly used for large steam-generating plants, should not be expected to be good sources of germanium because all the ash is carried along with the products of combustion. Chain-grate or other stoker types of installations are more likely to concentrate germanium in the fly ash because the fly ash forms only a small proportion of the total ash.

PART II. SPECTROCHEMICAL PROCEDURE

by
Juanita Witters

The spectrochemical method herein described provides for the determination of 0.01 to 0.08 percent of germanium oxide occurring in fly ash from coal. It is a preliminary stage in our effort to develop an analytical method that will be free of composition effects. The spectrochemical method provides a basis for selection of samples whose compositions show a significant effect on germanium line intensity. The method can be used for quantitative analysis with calibration checks for samples having a composition not covered by the current composition study.

Outline of Method

The steps in the procedure were developed from a method suggested by Kenneth B. Thomson of this laboratory. The composition of each sample is determined by a preliminary semiquantitative D.C. arc excitation. Bismuth as Bi_2O_3 is then added to the fly ash as an internal standard and the powder mixture is packed in a shallow annular cavity in a graphite electrode. The high-voltage A.C. arc spectrum is photographed. All exposures are step-sectored to provide an intensity calibration. Analytical calibration is provided by additions of GeO_2 to samples selected to cover the composition range encountered.

Apparatus

Commercially available spectrographic equipment is used with modification as indicated.

1. Excitation source. - The source of excitation is a modified 4600-volt A.C. arc unit of a National Spectrographic Laboratories, Inc., "Spec Power."

2. Spectrograph. - The spectrograph is a Bausch and Lomb large quartz Littrow, having a nominal reciprocal linear dispersion of 5 A per mm at 3200 A.

3. Recording equipment. - The spectrum is recorded on an Eastman Kodak 33 plate. Five stepped exposures are taken on a 4 by 10 inch plate.

4. Microphotometer. - The transmittances of the spectral lines are measured with a Jarrell-Ash JA-200 nonrecording microphotometer.

5. Developing equipment. - The plate is processed in a thermostatically controlled rocking developing machine, washed in running water, and dried in a warmed air stream.

6. Sample preparation equipment. - Samples are ground and mixed by a motor-driven mullite pestle and mortar.

Procedure

Standard samples. - All standards are prepared by adding chemically pure GeO_2 (Bi not detected) to similar uniform portions of fly ash samples. A series of such additions are made to each of several samples selected to cover the range of composition of the samples submitted for analysis, the range having been determined by a preliminary semiquantitative D.C. arc excitation and analysis. For each such sample a minimum of three additions are made, equivalent to about 1/2 X, X, and 2X percent GeO_2, where X percent GeO_2 is equivalent to the Ge spectrochemically observed. One part Bi_2O_3 (reagent grade; Ge not detected) is added to 29 parts ash to serve as an internal standard. Stocks of GeO_2 and of Bi_2O_3 are hand-ground in a mullite mortar and pestle to pass a 200-mesh silk screen.

A preliminary mixture of ash plus 1 percent GeO_2 is made by adding 30.0 mg GeO_2 to 2.970 gm of ash. The mixture is tumbled in a stoppered vial, then ground and mixed to sufficient uniformity. Separate portions are then diluted with ash and Bi_2O_3 added to form the three or more desired addition standards. (Erratic location of the four or more calibration points obtained would suggest an insufficient blending of GeO_2 in the preliminary mixture or errors in subsequent weighing.) If the desired addition level is less than .01 percent GeO_2, two separate preliminary mixtures of 1 percent and 3 percent added GeO_2 are made. Each becomes the head of a decade dilution series carried down to the required addition level.

Sample preparation. - The amounts of sample submitted have ranged from about 200 grams to a few kilograms. The entire sample is transferred to a large sheet of clean brown paper. Any lumps are removed to a mullite mortar, crushed, and returned. The sample is gently rolled and tumbled on the paper about three times the period required for visible uniformity. One or more portions of about 15 grams is removed. Use of two or more portions as separate samples shows the analytical uniformity at this stage. The sample is quartered by parting, opposite quadrants retained, retumbled, and again parted. Conventional quartering apparatus is avoided because of possible loss of fly-ash fines, which might be expected to be richer in Ge than the sample mean. One part Bi_2O_3, ground to pass 200-mesh, is added to 29 parts of dry ash. Heating or

re-ashing of the sample at this stage is avoided in view of the controversial possibility of loss of germanium by volatilization.

Electrode system. - The lower sample-containing electrode is formed by cutting regular grade graphite electrode stock 3/16-inch in diameter to form an annular cavity of which the depth, width, and center post diameter are each about 1 mm.

To load the lower electrode a quantity of sample, analytical or standard, is mixed with a few drops of anisole saturated with collodion to form a thick paste, and packed into the crater (using a stainless steel spatula). The paste is easier to handle than an untreated sample, and allows the loaded electrode to be more freely handled. After the anisole is evaporated (in a slightly warm oven if desired), the sample is sufficiently bound in the cavity to eliminate mechanical loss before the early cycles of the A.C. arc fuse the load.

The upper electrode is a 1/4-inch high-purity graphite rod shaped to a cone of about 90° included angle. Two to four lower electrodes are arced in turn against one upper electrode for each exposure. The electrode gap of 2.0 mm is reset for each electrode pair and no adjustment is made during arcing. The used end of the upper electrode is renewed by cutting off at least 1/8 of an inch above the base of the conical tip and reshaping it. One end only is shaped to avoid contamination within the hollow shaft of the chuck.

Excitation. - Nominal voltage - 4,600 volts
Nominal current - 1.6 amperes
Number of discharges per second - 120
Draft on source, lamp bank, and hood.

Exposure. - Spectral region - 2,400 to 3,400 A
Slit width - 20 microns
Sector speed - beyond flicker
Source warm-up - 10 seconds before the first exposure for each plate
Arc pre-burn period - none
Arc exposure period - two superposed 5-second exposures (or four superposed 5-second exposures for low Ge).

Photography. - Emulsion calibration: Each plate is calibrated for the two wave-length regions used by measuring two or more steps of the analytical and internal standard lines, supplemented by neighboring lines as needed.

Photographic processing: Emulsion - Eastman Kodak 33
Development - Eastman D11, rocked for 5 minutes at 68° C ± 0.5° F.
Fixing - Kodak acid fixer 15 minutes (at least twice the clearing time)

Photometry. - Transmittance measurements are made with the microphotometer for the analytical lines and the internal standard lines shown in table 1, supplemented by neighboring lines as needed, to calibrate for intensity. Measurements are confined as far as possible to those sections of the stepped lines for which meter readings lie within the straight-line portion of the response curve. For analyses near the limit of detection, samples and standards are re-arced using four 5-second exposures. Any analyses appearing near the upper limit could be brought into range by diluting that ash with an ash of similar

gross composition, or by using other less sensitive Ge lines. For calibration purposes, five replicate exposures are made for each standard, distributed among five plates and the five exposure positions. For analyses, duplicate exposures are made, distributed over two plates and two positions, with a third exposure taken in case of differences larger than expected from the precision.

Table 1. - Analytical and Internal Standard Lines Used

Analytical A	Int. Std. A	Concentration Range % GeO_2	Concentration Index % GeO_2
Ge 2651.1	Bi 2627.9	0.005-0.08	0.0542
Ge 3039.0	Bi 2993.3	0.01-0.15(?)	0.114

Precision

Precision may be calculated from the 5-fold standard replication, and for the 2- or 3-fold analysis replication. The data for the two classes are shown in tables 2 and 3, respectively. In table 2 the difference between the adopted values and the mean for each mixture shows the linearity of the calibration for each line pair. From data in table 2 we decided to use the mean of results from the two pairs of lines as a measurement. Entries in table 3 show these measurements for two trials for all the fly ash samples submitted for analysis whose germanium content was within the analytical range.

For convenience, calibrations were made in terms of percentage of GeO_2 and results so reported. This is not intended to imply that the germanium observed was known to be present as GeO_2.

Accuracy

If no bias has entered into the analysis, if the sample lots or portions analysed are representative of the entire sample submitted, and if no composition effect has been encountered, the accuracy should be comparable to the precision.

Table 4 shows the results obtained for five samples selected as addition bases using 1) self-calibration (addition of GeO_2 to same sample), and 2) the calibration obtained from adding GeO_2 to SP-94. Only SP-79 is considered to show a possible composition effect.

Table 5 shows the results obtained for three separate portions of four samples. Samples SP-79 and SP-80 were members of the sample group SP-79 to 86, which were not homogeneous in appearance as received. Samples SP-94 and SP-109 were members of the sample group SP-94 to 109, which were homogeneous in appearance. From the results it is assumed that the sampling procedure has been adequate.

Seven samples received, SP-400 through SP-406, showed values of GeO_2 below the analytical range (0.01-0.08 percent GeO_2) claimed for the method. For such lower values, the standard two 5-second exposures are changed to four 5-second ones. The uncertainty for six of these samples is shown in table 6. The coefficient of variation of 9 percent is biased, with lower values obtained by use of the standard two 5-second exposures below the analytical range. The seventh

Table 2. - Precision from Addition Standards

Percentage of GeO_2 added to SP-94 + Bi_2O_3		Concentration of GeO_2 (%)			
		Ge 2651 Bi 2627	Ge 3039 Bi 2993	Mean	Adopted
None		0.0208	0.0215	0.0212	
		0.0220	0.0210	0.0215	
		0.0223	0.0220	0.0222	
		0.0210	0.0228	0.0219	
		0.0190	0.0215	0.0202	
	Av.	0.0210	0.0218	0.0214	0.0210
	V* =	(6.2%)	(2.2%)	(3.6%)	
0.0100		0.0303	0.0297	0.0300	
		0.0315	0.0313	0.0314	
		0.0292	0.0293	0.0292	
		0.0314	0.0341	0.0328	
		0.0293	0.0313	0.0306	
	Av.	0.0303	0.0311	0.0308	0.0310
	V* =	(2.2%)	(6.1%)	(3.5%)	
0.0200		0.0417	0.0385	0.0401	
		0.0435	0.0400	0.0418	
		0.0453	0.0400	0.0405	
		0.0410	0.0422	0.0416	
		0.0390	0.0405	0.0398	
	Av.	0.0421	0.0402	0.0408	0.0410
	V* =	(5.7%)	(3.3%)	(2.2%)	
0.0400		0.0570	0.0580	0.0575	
		0.0605	0.0590	0.0598	
		0.0605	0.0615	0.0610	
		0.0610	0.0630	0.0620	
	Av.	0.0598	0.0604	0.0601	0.0610
	V* =	(3.1%)	(3.8%)	(3.2%)	

* $V = \frac{100}{C}\sqrt{\frac{\Sigma d^2}{n-1}}$

where V = coefficient of variation.
C = concentration.
d = difference between measurement and mean.
n = number of replications.

Table 3. - Precision from Duplicated Analytical Samples

Sample ($+ Bi_2O_3$)	Concentration ($\% GeO_2$) Trial 1	Trial 2
SP-79A	0.0124	0.0125
79B	0.0108	0.0114
80A	0.0138	0.0133
80B	0.0126	0.0130
81	0.0365	0.0377
83	0.0422	0.0388
84	0.0431	0.0416
85	0.0335	0.0346
86	0.0255	0.0268
94A	0.0218	0.0205
94B	0.0215	0.0199
95	0.0352	0.0372
96	0.0348	0.0320
97	0.0250	0.0260
98	0.0302	0.0295
99	0.0320	0.0350
100	0.0318	0.0328
101	0.0342	0.0368
102	0.0378	0.0385
103	0.0435	0.0435
104	0.0408	0.0415
105	0.0418	0.0385
106	0.0360	0.0335
107	0.0315	0.0355
108	0.0405	0.0360
109A	0.0468	0.0458
109B	0.0460	0.0460

$$V = 100 \sqrt{\frac{\Sigma (d/C)^2}{2n}} = 4.2\%$$

where V = coefficient of variation
C = concentration
d = difference between pair measurements
n = number of pairs

Table 4. - Comparison of Separate Calibrations

Sample	Concentration of GeO_2 (%) By addition of GeO_2 to sample	By addition of GeO_2 to SP-94
SP-79	0.0124	0.0151
80	0.0131	0.0134
81	0.036	0.037
98	0.030	0.029
109	0.047	0.046

Table 5. - Comparison of Analyses of Separate Portions of Samples

Sample	Concentration of GeO_2 (%) Portion A	Portion B	Portion C
SP-79	0.0124	0.0114	0.0110
80	0.0135	0.0133	-
94	0.0212	0.0208	0.0209
109	0.0463	0.0460	0.0461

sample, SP-404, showed 0.001 percent GeO_2 as run by a D.C. arc method used for coals and ash other than fly ash. For this method, the limit of detection is 0.0005 percent GeO_2.

Table 6. - Relative Accuracy Below the Analytical Range

Sample	Concentration of GeO_2 (%)	
	Four 5-second exposures	Two 5-second exposures
SP-400	0.0105	0.0093
401	0.0043	0.0033
402	0.0051	0.0044
403	0.0090	0.0086
405	0.0090	0.0086
406	0.0084	0.0080

$$V = 100 \sqrt{\frac{\Sigma (d/C)^2}{2n}} = 9.2\%$$

where V = coefficient of variation
C = concentration
d = difference between pair measurements
n = number of pairs

For the range below 0.010 percent GeO_2, self-calibration becomes necessary to maintain an estimated accuracy of 0.001 percent GeO_2. It is considered possible that the background, undetected and hence uncorrected, may become significant below 0.010 percent GeO_2. For samples in this lower range a superposed exposure of 3 minutes between high-purity electrodes was needed to bring up to measurable amounts the background beside the lines used. Measurements on the 3-minute graphite arc spectrum alone provided a correlation between the background added beside the analytical lines and that added under the analytical lines. This background correction lowered the value of GeO_2 by 0.001 percent, the uncertainty claimed for the method.

In the foregoing method development the following assumptions were made: 1) Germanium was present as GeO_2, 2) the concentration-intensity response was linear, 3) the background was negligible, and 4) any loss during sample or standard mixing was nonselective.

Sample and standards for the methods used in this laboratory were the same to at least 99.9 percent for each of six samples, because the sample itself was used as the standard base for an addition series.

Background was not detectable for either the two 5-second or the four 5-second exposures for either line-pair neighborhood.

Except for one of the two low-concentration samples, the results were consistent for addition bases containing a 2- to 4-fold range of GeO_2 values. Background corrections would be expected to affect most the analyses of samples containing the least Ge, might be different for different ashes, and probably would be different for the two line pairs used. It seems unlikely that consistent results could be obtained for two line-pair measurements for five or six sam-

ples of 2- to 4-fold different concentration if undetected background were significant.

The precision of the A.C. arc is dependent on reproducible volatilization of the sample from the electrode as well as on reproducible excitation of the material in the analytical gap. Accordingly, arcing to exhaustion is to be avoided with the A.C. arc source with which the exposure period is confined to a period of reproducible emission for analytical element and internal standard. Increasing the arcing period beyond this condition brings about erratic results. The period used was selected from trials made for two 5-second, four 5-second, one 10-second, two 10-second, and one 20-second exposures.

Selection of a proper internal standard makes the arcing period a less critical factor.

Summary

With the spectrochemical method described for use of the high voltage A.C. arc for the analysis of germanium in fly ash, a precision of 4 percent is obtained for the analytical range from 0.01 to 0.08 percent GeO_2. For lower values down to 0.004 percent GeO_2, the precision of 10 percent accuracy is considered comparable.

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